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Mechanisms of Simultaneous Hydrogen Production and Formaldehyde Oxidation in H_2O and D_2O over Platinized TiO_2

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ABSTRACT

The simultaneous photocatalytic degradation of formaldehyde and hydrogen evolution on platinized TiO_2 have been investigated employing different mixtures of H_2O-D_2O under oxygen free conditions using Quadrupole Mass Spectrometery (QMS) and Attenuated Total Reflection Fourier Transformed Infrared spectroscopy (ATR-FTIR). The main reaction products obtained from the photocatalytic oxidation of 20% formaldehyde were hydrogen and carbon dioxide. The ratio of evolved H_2 to CO_2 was to 2 to 1. The HD gas yield was found to be dependent on the solvent and was maximised in a mixture of H_2O:D_2O (20%:80%). The study of the solvent isotope effect on the degradation of formaldehyde indicates that the mineralization rate of formaldehyde (CO_2) decreases considerably when increasing the concentration of D_2O. Based on the ATR-FTIR data, the formaldehyde in D_2O is gradually converted to deuterated formic acid during UV

irradiation which was confirmed by different band shifting. An additional FTIR band at 2050 cm^{-1} assigned to CO was detected and was found to increase during UV irradiation due to the adsorption of molecular CO on Pt/TiO_2. The results of these investigations showed that the molecular hydrogen is mainly produced by the reduction of two protons originating from water and formaldehyde. A detailed mechanism for the simultaneous hydrogen production and formaldehyde oxidation in D_2O is also presented.

KEYWORDS: *Pt/TiO_2, Hydrogen Production, D_2O, Formaldehyde, Photocatalytic reaction.*

INTRODUCTION

Simultaneous production of hydrogen with degradation of organic pollutants has been a subject of intense global research interest since it could address the issues of both energy sustainability and environmental remediation at the same time.[1,2] In both applications, photocatalytic reactions are initiated by exciting electrons from the valence band (VB) to the conduction band (CB) at the TiO_2/water interface or in the bulk of the TiO_2 particles following UV irradiation. Although both applications are based on the same photoinduced charge transfer occurring on TiO_2 particles, sacrificial agents play a significant role as an electron donor/acceptor for photocatalytic degradation reactions and hydrogen production. The photocatalytic degradation process involves the formation of reactive oxygen species (ROS) which can oxidize and degrade organic compounds. In this case, trapped electrons are readily scavenged by adsorbed molecular oxygen which is essential to achieve the mineralization under aerated conditions. On the other hand, photocatalytic hydrogen production takes place under oxygen free conditions which is achieved by photogenerated electrons, provided that their energy is sufficient to reduce protons to hydrogen molecules.[3] In other words, the photocatalytic degradation of pollutants is initiated by a single electron transfer whereas the hydrogen production is carried out via a two electron transfer process.

To achieve dual-function photocatalysis, the photocatalyst TiO_2 should be able to oxidize organic substrates with protons as an electron acceptor.

A large variety of organic compounds such as methanol, ethanol, acetic acid and acetaldehyde, have been used as sacrificial reagents which provides an efficient electron/hole separation due to the fact that it reacts irreversibly with photogenerated holes, resulting in higher quantum efficiencies.[3,4] Indeed, the photogenerated holes can either react with surface Ti–OH groups, adsorbed water producing •OH radicals or they might be transferred directly to adsorbed organic molecules. Different studies have demonstrated that the continued addition of electron donors (sacrificial agents) is required effective hydrogen production at the semiconductor conduction band with a consequential simultaneous degradation of the electron donating agent, such as an organic substrate, via the valence band reaction.[5,6] Since the competitive reactions may take place between the adsorption of water and organic compounds on TiO_2 surfaces, the primary events and the source of molecular hydrogen formed during oxidation of organic molecules have not yet been clearly determined. In order to get a better understanding of the reaction mechanisms under aqueous conditions, a simple system is advantageous so formaldehyde has been chosen as a model pollutant.

In this work, details of the mechanism of the photocatalytic hydrogen evolution on platinized TiO_2 from aqueous formaldehyde solutions in a different concentration of D_2O have been investigated. The effect and the role of D_2O adsorption on the photocatalytic activity have been considered. Particular attention has focused on the mechanisms of hydrogen production to determine whether the origin of the evolved molecular hydrogen is from water or formaldehyde. The photocatalytic degradation mechanism of formaldehyde in D_2O was elucidated based on the QMS spectrometer and further confirmed by ATR-FTIR spectroscopy data.

EXPERIMENTAL SECTION

Materials

Platinized TiO_2 photocatalyst powders (1 wt% Pt) were kindly supplied by H.C. Starck. Formaldehyde solution (37 wt. % in H_2O) and Deuterium oxide (D_2O) (99.9 atom% D) were purchased from Sigma Aldrich. Deionized water (H_2O) was supplied from a Millipore Mill-Q system with a resistivity equal to 18.2 Ω cm at 25 °C.

Photocatalytic activity measurements

Quadrupole mass spectrometer

The photocatalytic reactions were carried out in an experimental setup consisting of a gas supply, a mass flow controller, a 100 cm^3 double jacket Duran and/or a quartz glass reactor with in-and outlets, and a quadrupole mass spectrometer (QMS) for gas analysis (Hiden HPR-20). The system was continuously purged with argon as carrier gas, the Ar flow was controlled by a mass flow controller (MFC) as schematically shown in Figure 1.[6]

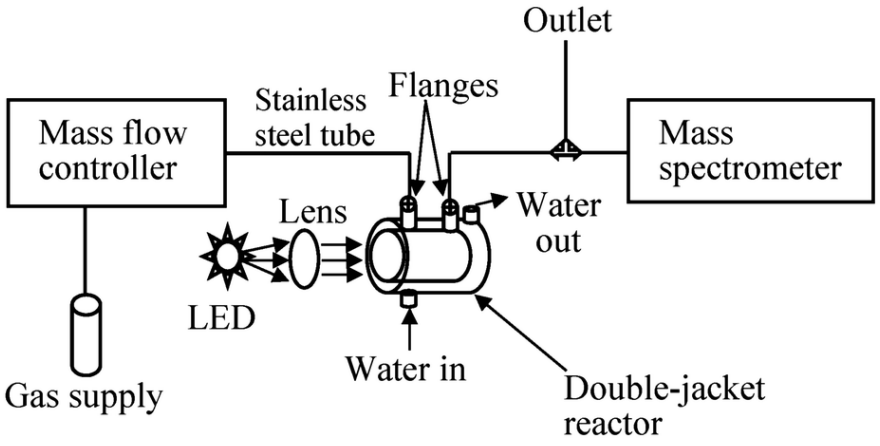


Figure 1. Experimental setup for the measurement of the photocatalytic H_2 and CO_2 evolution. (Copyright 2014 Royal Society of Chemistry.)

In a typical run, 0.05 g of the photocatalyst Pt/TiO_2 were suspended in 50 mL of an aqueous 20% formaldehyde solution by sonication. The suspension was transferred into the photoreactor and

purged with Ar for 30 min to remove dissolved O_2. Afterwards, the reactor was connected to the mass flow controller and to the Q/C capillary sampling inlet of the QMS through metal flanges and adapters. To remove the air in the headspace of the reactor, an Ar gas stream was continuously flowed through the reactor before irradiation, until no traces of molecular oxygen or nitrogen could be detected by the QMS. The Ar gas flow rate through the reactor was kept constant at 10 cm^3 min^{-1} during the photocatalytic experiments. The inlet flow rate/gas consumption by the QMS was 1 cm^3 min^{-1} and the excess gas was directed towards the exhaust. The sampling rate of the QMS was in the millisecond time range, thus allowing a fast tracking of the reaction. After stabilization of the system background, the reactor was irradiated from the outside using Xenon lamp (light intensity 30 $mWcm^{-2}$). For quantitative analysis of H_2 and CO_2, the QMS was calibrated employing standard diluted H_2 and CO_2, respectively, in Ar (Linde Gas, Germany).

ATR-FTIR Spectroscopic

Initially, an aqueous suspension of platinized TiO_2 at a concentration of 5 g L^{-1} was prepared and sonicated for 15 min in an ultrasonic cleaning bath. An aliquot of 400 µL of the TiO_2 suspension was placed on the surface of the ZnSe ATR crystal and this small volume was simply spread by balancing the unit manually. The suspension was then evaporated to dryness by storing the crystal in a semi-opened desiccator at room temperature. Prior to deposition of the TiO_2 films, the ZnSe surfaces (area = 6.8 mm×72 mm) were cleaned by polishing with 1 mm diamond paste (Metadi II, polishing grade) and rinsed with methanol and deionised water. The coverage of the final dry layer of particles obtained was 2.3 g m^{-2} and the layer appeared to be very homogeneous under visual inspection. In the original preparation by Hug *et al*, Atomic Force Microscopy (AFM) measurements of layers with coverage of 2.3 g m^{-2} yielded a thickness of 1-3 µm.[7] The final

resulting layers of particles remained stable over the entire course of the experiment. Thus, it was assumed that the effective path lengths at all wavelengths remained unchanged.

The ATR-FTIR spectra of the TiO_2 samples were monitored by a FTIR spectrometer (IFS 66 BRUKER) equipped with an internal reflection element 45º ZnSe crystal and a deuterated triglycine sulfate (DTGS) detector. The interferometer and the infrared light path in the spectrometer were constantly purged with Argon and nitrogen to avoid H_2O and CO_2 contamination. The spectra were recorded with 300 scans at 4 cm^{-1} resolution and analyzed using OPUS version 6.5 software. Irradiation of samples with UV(A) light were carried out using an LED lamp (Model LED-Driver, THORLABS) emitting UV light (365 nm). The distance from the UV lamp to the surface of the test solution was kept at 30 cm on which the intensity of UV(A) light was 1.0 $mWcm^{-2}$ measured by a UV radiometer (Dr. Honle GmbH, Martinsried, Germany).

RESULTS

The photocatalytic reactions of formaldehyde were examined by the Quadrupole Mass Spectrometer (QMS) and Attenuated Total Reflection Fourier Transformed Infrared spectroscopy (ATR-FTIR). The QMS experimental setup shown in Figure 1 allowed in line monitoring of the entire course of the reaction with the advantage of simultaneously detecting several gaseous compounds formed during the photocatalytic reaction. Figure 2 shows the time course of the photocatalytic H_2 and CO_2 evolution from photoxidation of a 20 vol% formaldehyde in aqueous solution at pH 3.2. Before starting UV illumination, the time course of the investigated gaseous compounds was monitored in the dark for 60 min until their signals became stable. Typical results of QMS analysis in the photocatalytic reaction revealed that after the light was switched on, the evolved gases such H_2 and CO_2 were observed and reached the region with different constant evolution rates. The H_2 and CO_2 evolution rates were determined from the difference between the

baseline (at the end) and the average of all measuring points obtained in the middle part of the curve (steady state region). Besides the evolution of H_2 and CO_2, traces of CO gas were also detected with constant evolution rates (Table S1. Supporting Information). Additionally, as shown in Figure 2, the evolution rates of H_2 and CO_2 gas were observed to be regular and steady during oxidation of formaldehyde within a period of 6 hours. However, the amount of evolved molecular hydrogen was found to be more than double that of the quantity of CO_2 generated. The rates for H_2 and CO_2 evolution were determined to be 54 and 24 µmol h^{-1}, respectively. It was assumed that the photocatalytic oxidation of formaldehyde occurred according to Eq. (1), where the ratio of evolved H_2 to CO_2 is 2 to 1.

$$HCHO + H_2O \xrightarrow{Pt/TiO_2} CO_2 + 2H_2 \qquad (1)$$

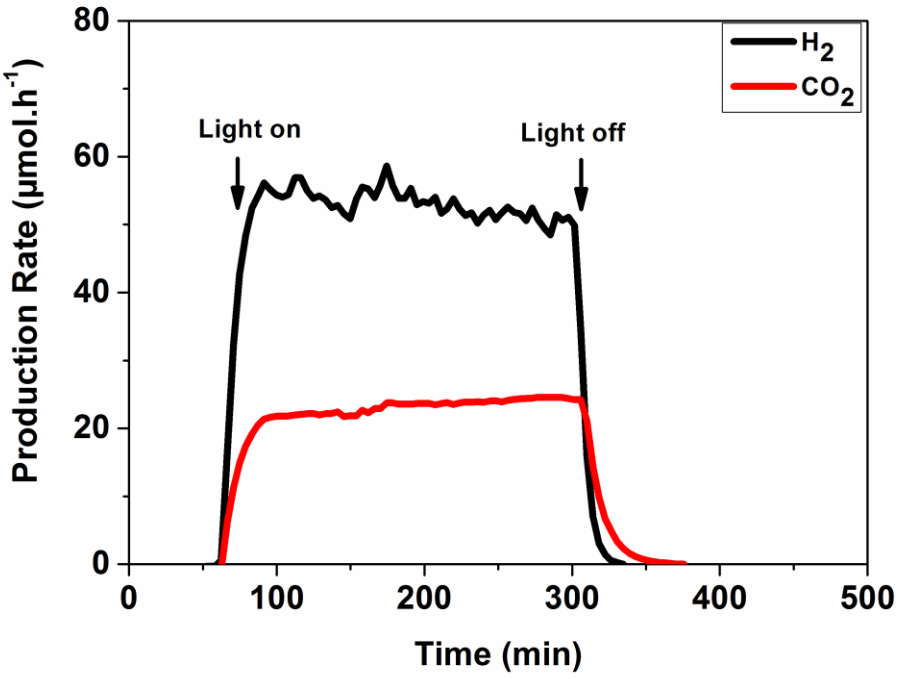


Figure 2. Photocatalytic H_2 and CO_2 evolution on platinized TiO_2 from 20 vol% formaldehyde solution: 0.5 gL^{-1} Pt/TiO_2, 50 mL suspensions, and UV illumination employing Xenon lamp (light intensity 30 mW cm^{-2}).

In order to understand the mechanism of the photocatalytic degradation of formaldehyde as well as to identify the origin of the evolved hydrogen gas, a series of photocatalytic degradations of formaldehyde on platinized TiO_2 were performed for 6 h under UV irradiation at different concentrations of D_2O. Table 1 shows the photocatalytic of H_2, D_2 and HD gas evolution from a 20 vol% aqueous formaldehyde solution in different concentrations of D_2O. The evolution of H_2, D_2 and HD gas were detected by a mass spectrometery (QMS).

Table 1. Photocatalytic evolution of H_2, D_2 and HD on platinized TiO_2 from 20 vol% formaldehyde solution: 0.5 gL^{-1} Pt/TiO_2, 50 mL suspensions, and UV illumination employing Xenon lamp (light intensity 30 mW cm^{-2}).

Experiments	**H_2 (a.u.)**	**D_2 (a.u.)**	**HD (a.u.)**
0% D_2O	2.2	0	0
20% D_2O	1.7	0.002	0.1
40% D_2O	1.4	0.01	0.3
60% D_2O	0.9	0.03	0.4
80% D_2O	0.2	0.2	0.6

It is clearly seen from table 1 that the photocatalytic H_2 evolution significantly decreased with increasing D_2O concentration. At the same time, the amount of HD and D_2 increased. Additionally, the amount of evolved HD was found to be rather high compared to D_2. The typical time courses of the photocatalytic H_2, HD and D_2 evolution rates from aqueous formaldehyde in H_2O-D_2O mixture (20%:80%) is shown in Figure 3. It is clearly seen that the signal of the appropriate gaseous

compound increased directly after the lamp was switched on. Then the evolved gases, such as H_2, D_2 and HD reached peak with different constant evolution rates. When the light was switched off, the gas evolution rate rapidly decreased reaching the baseline of the corresponding compounds in the system. Interestingly, although the photocatalytic reaction was performed in 80% of D_2O, the increases of evolved HD was much higher than D_2 gas. These results clearly show the effect of solvent in the formation of molecular hydrogen during photocatalytic oxidation of formaldehyde.

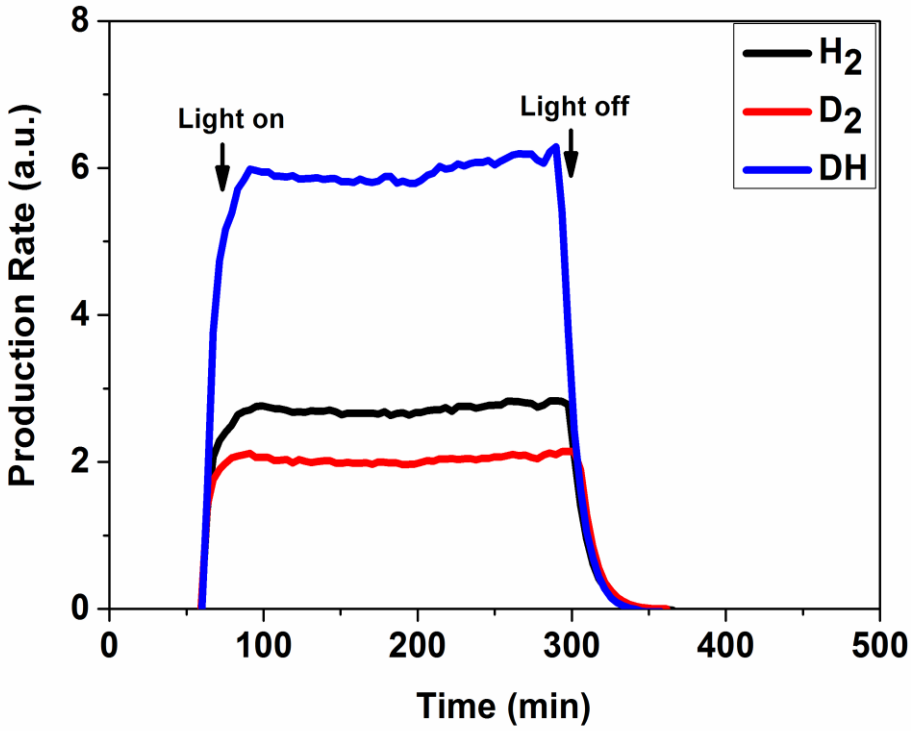


Figure 3. Photocatalytic H_2, D_2 and HD evolution in H_2O-D_2O mixture (20%:80%) on platinized TiO_2 from 20 vol% formaldehyde solution: 0.5 gL^{-1} Pt/TiO_2, 50 mL suspensions, and UV illumination employing Xenon lamp (light intensity 30 mW cm^{-2}).

Furthermore, D_2O is expected to have an influence on the photocatalytic mineralization rate of formaldehyde on platinized TiO_2 under UV irradiation which occurs simultaneously with the isotopic hydrogen evolution which were shown in table 1. Figure 4 shows the photocatalytic

evolution rate of CO_2 in H_2O at different concentrations of D_2O on Pt/TiO_2. It is obvious from Figure 4 that the constant evolution rates of CO_2 have decreased gradually by increasing the concentration of D_2O. The formation of CO_2 confirms the complete mineralization of formaldehyde through the oxidation of intermediates. The mineralization rate of formaldehyde (CO_2), however, was significantly reduced when the photocatalytic reaction was conducted in the D_2O solvent. Based on these results, we suggest that the adsorption of H_2O/D_2O plays a crucial role in photocatalytic reactions which may act as electron donors and electron acceptors for simultaneous hydrogen production and formaldehyde oxidation over platinized TiO_2.

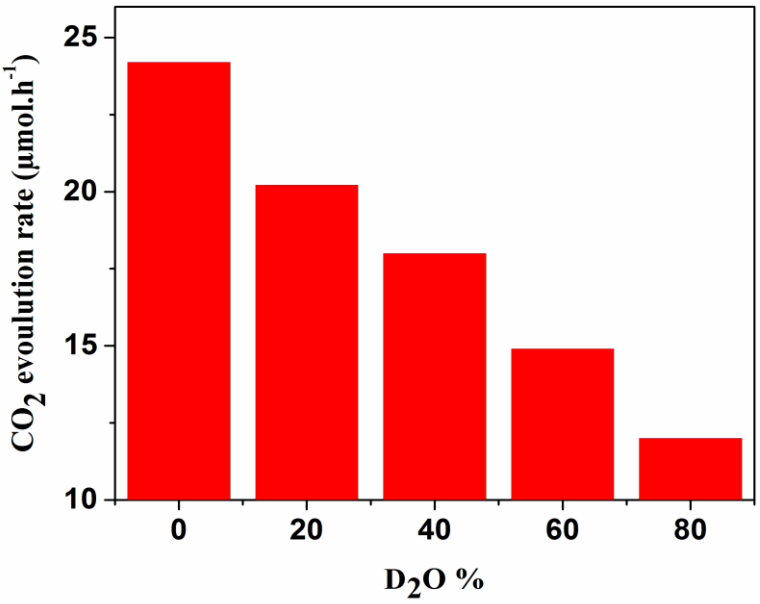


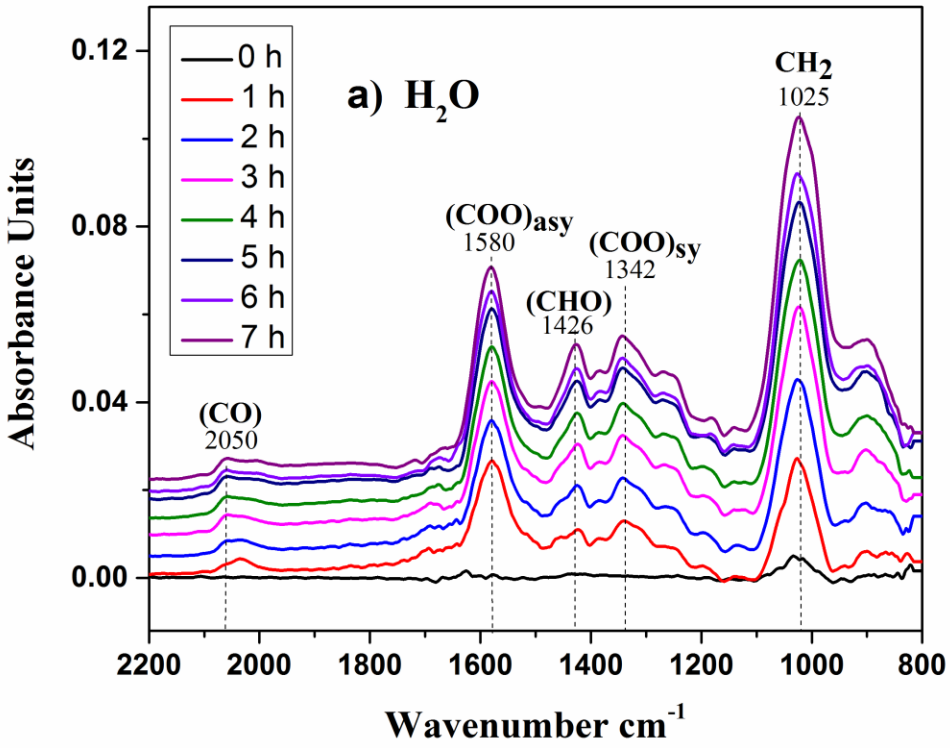
Figure 4. Photocatalytic CO_2 evolution rate in H_2O with different concentration of D_2O on platinized TiO_2 from 20 vol% formaldehyde solution: 0.5 gL^{-1} Pt/TiO_2, 50 mL suspensions, and UV illumination employing Xenon lamp (light intensity 30 mWcm^{-2}).

For a better understanding of the reaction mechanism of this process at the platinized TiO_2/aqueous solution interface, the adsorption behaviour of formaldehyde on TiO_2 surfaces under UV irradiation was investigated by *in situ* ATR-FTIR spectroscopy. The time evolution of the adsorbed

20% formaldehyde spectra on Pt/TiO_2 at pH 3.2 were performed in the dark for 2 h in pure water (a) and H_2O–D_2O mixture (20%:80%) (b), (Figure S1. Supporting Information). The FTIR spectra are reported in Absorbance, having subtracted the spectrum of pure H_2O (D_2O) as background. The spectrum of formaldehyde adsorption shows different IR absorbances at 1025, 1248, 1435 and 2912 cm^{-1} which are assigned to different types of CH_2 vibrations [8,9,10] (Figure S1-a Supporting Information). When D_2O was used instead of pure water as a background, the typical bands assigned to formaldehyde were also observed (Figure S1-b. Supporting Information). Since the concentration of 20 vol% aqueous formaldehyde solution was prepared in water, the bands at 3400 cm^{-1} and 1450 cm^{-1} were observed and assigned respectively to the OH stretching mode band of water and the isotopologue HDO bending band at 1450 cm^{-1} where the band attributed to the scissor modes of the CH_2 at 1435 cm^{-1} overlapped.[11]

Prior to UV(A) irradiation, the spectrum of formaldehyde adsorption under dark conditions was taken as reference background spectrum. Figure 5. shows the time evolution of the FTIR spectra recorded during the photocatalytic decomposition 20% formaldehyde in pure water (a) and H_2O–D_2O mixture (20%:80%) (b), respectively. The most striking feature here was the initially rapid upward shift in the baseline which was interpreted as transient and persistent diffuse reflectance infrared signals due to the population of conduction band electrons upon irradiation of TiO_2 particles.[12] Furthermore, it can be clearly seen from the figure (Fig. 5a) that during UV(A) illumination the formation of new bands at 1580, 1426 and 1342 cm^{-1} corresponding to $\nu_{asy}(COO-)$, δ (CHO) and $\nu_{sy}(COO-)$, respectively were observed.[13] The bands detected at 2050 cm^{-1} during UV irradiation have previously been assigned in the literature to CO on Pt in the "on-top" position.[14,15] Surprisingly, unlike the case of pure water, the band at 1426 cm^{-1} assigned to δ (CHO) was shifted to a lower frequency (1415 cm^{-1}), whereas the bands at 1580 cm^{-1} and 1342

cm^{-1}, assigned to asymmetric ν_{asy} (COO−) and symmetric ν_{sy} (COO−) stretching vibrations, shifted to higher values at 1590 cm^{-1} and 1348 cm^{-1} respectively (Fig. 5b). Furthermore, two bands observed at 1730 and 1668 cm^{-1} were assigned to carbonyl group with different vibration modes i.e., C=O, O-C=O.[13,16] As can be seen in Figure 5, the appearance of new bands can be considered as evidence for such adsorption intermediates being formed during oxidation of formaldehyde which is most likely to be attributed to a photocatalytically generated formate/formic acid. These results indicate that the photocatalytic reactions and the behavior of formate/formic acid formed, however, is strongly influenced by deuterium water (D_2O).



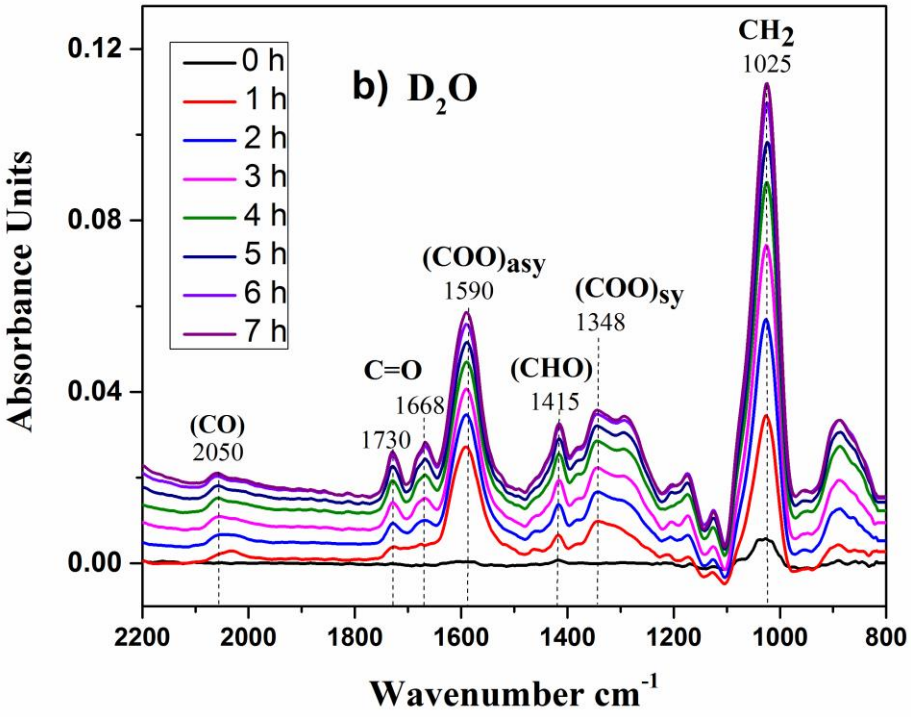


Figure 5. Time evolution of the ATR–FTIR spectra of adsorbed Formaldehyde a) in pure water, b) in H_2O-D_2O mixture (20%:80%) on platinized TiO_2 under 7 h of UV(A) illumination.

DISCUSSION

The photocatalytic hydrogen production over platinized TiO_2 during oxidation of formaldehyde was examined by the quadrupole mass spectrometer (QMS). It is well known that formaldehyde acts as an electron donor or a so-called sacrificial reagent for the photocatalytic H_2 production at the surface of Pt/TiO_2. It is obvious from Figure 2 that the amount of evolved molecular hydrogen was two times higher than that of the quantity of CO_2 that was generated. The ratio of H_2 to CO_2 that was evolved was found to be 2 to 1 (Eq. 1). It was reported that the photocatalytic activity of H_2 production depends strongly on various a range of experimental parameters including platinum deposition, catalyst concentration, pH and concentration of formaldehyde.[17] The effect of water adsorption, however, was expected in photocatalytic reactions which could be used protons as

electron acceptor for hydrogen production reactions. Isotopic studies show that different gases were evolved, namely H_2, HD, and D_2 which were formed during UV irradiation of the photocatalyst (table 1). These results clearly indicate the effect of solvent (D_2O) in molecular hydrogen formation during photocatalytic oxidation of formaldehyde. Interestingly, although the concentration of D_2O was higher (80%), the intensity of the signal assigned to HD increased and showed a maximum intensity during UV(A) illumination compared to the signal of D_2 (Figure 3). These results confirm that during photocatalytic oxidation of formaldehyde the protons from water molecule was involved as an electron acceptor to produce molecular hydrogen. The adsorption of D_2O was also found to play a role in the photocatalytic degradation of formaldehyde. As shown in Figure 4, the evolution rate of CO_2 produced during UV irradiation was found to be maximised in pure water, then decreased with the addition of increasing levels of D_2O. In our previous study we reported that the isotopic exchange during D_2O adsorption takes place on the surface of the photocatalyst in the dark by replacing hydroxyl groups adsorbed on the TiO_2 surface Eq. (2).[11]

$$\mathrm{Ti-OH} + \mathrm{OD^-} \longrightarrow \mathrm{Ti-OD} + \mathrm{OH^-} \qquad (2)$$

Thus, under UV illumination, the photogenerated valence band holes could oxidize the deuteride ions adsorbed at the surface forming •OD radicals. Since the isotopic exchange reaction occurred on the catalyst surface, the kinetic isotopic effect was expected during phototcatalytic reaction. The first primary kinetic solvent isotope effect on a photocatalytic oxidation reaction was reported by Cunningham and Co-author.[18] This behavior was confirmed by Robertson *et al.* who also proposed that the photocatalytic reactions take place on the catalyst surface rather than in the bulk of the solution.[19] As shown in figure 4, the reduced rate of photocatalytic activity was clearly observed in presence of D_2O. This result again confirms the role of the solvent as an electron donor which is involved in photocatalytic oxidation of formaldehyde. Robertson *et al.* proposed that the

reduced rate of photocatalytic degradation may have been due to •OD radicals having a lower oxidation potential when compared to •OH radicals.[20] It was reported however, both holes and hydroxyl radical acted as oxidizing species both directly and indirectly, for the degradation of formaldehyde.[17] Although the formation of CO_2 confirmed the complete mineralization of formaldehyde as the final oxidation, primary intermediate products were however generated during the photocatalytic process. In-situ ATR-FTIR studies of the photocatalytic reaction of formaldehyde revealed the formation of new bands of carboxylate groups at 1580 cm^{-1} and 1342 cm^{-1} which were assigned to the asymmetric ν_{asy} (COO−) and symmetric ν_{sy} (COO−) stretching vibrations of formate adsorption (Figure 5a). Sun *et al.* reported that the formaldehyde molecules could be adsorbed to the hydroxyl groups on the TiO_2 surface via hydrogen bonding. Under UV irradiation, however, the adsorbed formaldehyde rapidly converted to the formate species and adsorbed through the bridging bidentate structure.[21] Interestingly, when a H_2O-D_2O mixture (20%:80%) was used instead of pure water, the band at 1426 cm^{-1} assigned to δ (CHO) shifted to a lower frequency (1415 cm^{-1}) while the carboxylate band shifted to higher frequency (Figure 5b). Surprisingly, unlike the case of water, different vibration modes of carbonyl group were observed at 1730 cm^{-1} and 1668 cm^{-1} (Figure 5b). Taking into account, the pk_a value in D_2O should be higher than that in H_2O, the protonation of formic acid becomes more favorable in D_2O.[22] From these results we suggest that in the presence of D_2O the formaldehyde was most likely gradually converted to deuterated formic acid (HCOOD) during the photocatalytic reaction. It is worth noting that, a competitive reaction between the adsorption of H_2O/D_2O and formate/formic acid may occur during photooxidation of formaldehyde. Based on findings by Medlin *et al.* the adsorption of water induces the dissociation of formic acid to formate on Pt/TiO_2 surface. These transformations can have an important influence on elementary reaction steps and the rate of

photocatalytic decomposition of formic acid on Pt/TiO_2.[23] Our previous work revealed, however, that the isotopic exchange leads to a new constructive interaction between the adsorbate/intermediate and the OD group.[24,25] Due to the kinetic solvent isotope effect, we suggest that the oxidation of formaldehyde is mainly occurred directly by •OD radicals resulting deuterated formic acid (HCOOD) as an adsorbed intermediate. Subsequently, the deuterated formic acid adsorbed reacts through direct oxidation by valence band hole (photo-Kolbe reaction). Simultaneously, the photogenerated electrons reduce H^+ and D^+ originally coming from formaldehyde and D_2O to form molecular HD. The details of the proposed mechanism of simultaneous hydrogen production and formaldehyde oxidation in the presence of D_2O are presented in Eqs. (3–10):

$$Pt/TiO_2 \rightarrow e^-(Pt) + h^+(TiO_2) \quad (3)$$

$$D_2O + h^+ \rightarrow OD^\bullet + D^+ \quad (4)$$

$$HCHO + OD^\bullet \rightarrow HCOOD + H^\bullet \quad (5)$$

$$H^\bullet + h^+ \rightarrow H^+ \quad (6)$$

$$D^+ + H^+ + 2e^- \rightarrow HD \quad (7)$$

$$HCOOD + 2h^+ \rightarrow CO_2 + H^+ + D^+ \quad (8)$$

$$D^+ + H^+ + 2e^- \rightarrow HD \quad (9)$$

$$HCHO + D_2O \xrightarrow{Pt/TiO_2} CO_2 + 2HD \quad (10)$$

Moreover, the band observed at 2050 cm^{-1} during UV irradiation was assigned to the CO adsorbed on Pt in the "on-top" position.[14] Two different sources for CO gas formation can be explained by decarbonylation of formaldehyde or/and dehydration of formic acid.[26,27] Since the evolution rate

of H_2 (54 μmol h^{-1}) was more than twice that of CO_2 (24 μmol h^{-1}) according to figure 2, we suggest that the formation of CO is most likely caused by decarbonylation of formaldehyde Eq. (11).

$$HCHO \rightarrow CO + H_2 \qquad (11)$$

Nakahara *et al*. reported that Eq. (11) was based on the proton-transferred decarbonylation of formaldehyde, where one proton was intramolecularly transferred to the other proton attached to the same carbonyl group to form a hydrogen-hydrogen bond, followed by the carbonyl group elimination through a breakage of two hydrogen-carbon bonds resulting carbon monoxide and hydrogen.[28] It seems likely, however, that the photocatalytic oxidation of formaldehyde was the dominant pathway for hydrogen production.

CONCLUSION

The effect of D_2O on the photocatalytic H_2 and CO_2 evolution during the degradation of 20% formaldehyde has been extensively studied using different concentrations of D_2O (0-80%). The experimental results have shown clearly the role of solvent in both hydrogen production and formaldehyde oxidation as an electron acceptor (protons) and electron donor respectively. The solvent isotopic effect indicated that the photocatalytic oxidation of formaldehyde was found to take place through •OH radicals at the valence band while the photocatalytic hydrogen production was mainly occurred at the conduction band by the reduction of two protons originating from water and formaldehyde.

ASSOCIATED CONTENT

Supporting Information.

The Supporting information is free of charge on the ACS Publications website at xxxx.

Additional data, including, Evolution of traces of CO gas (Table S1.), ATR–FTIR spectra of adsorbed Formaldehyde in the dark (Figure S1.), Absorption spectrum of suspended TiO_2 particles in water and irradiance of Xenon lamp (Figure S2.).

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Notes

The authors declare no competing financial interest

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